

Surface Dynamics of a Freely Standing Smectic-A Film

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(February 1, 2008)

Abstract

A theoretical analysis of surface fluctuations of a freely standing thermotropic smectic-A liquid crystal film is provided, including the effects of viscous hydrodynamics. We find two surface dynamic modes (undulation and peristaltic). For long wavelengths and small frequencies in a thin film, the undulation mode is the dominant mode. Permeation enters the theory only through the boundary conditions. The resulting power spectrum is compared with existing experiments. It is also shown that feasible light scattering experiments on a freely standing smectic-A film can reveal viscosity and elastic coefficients through the structure of the power spectrum of both the undulation and peristaltic modes.

61.30.Gd, 68.15.+e, 83.70.Jr

Recent experiments on dynamics and instabilities of soap [1] and smectic-A films [2] have raised interest in the general question of dynamics of freely-standing films. The interactions between bulk elasticity and surface tension make freely-standing smectic-A films (FSSF) suitable systems for studying finite-size and surface effects; hence, fluctuations in FSSF are an important subject for both theoretical and experimental study [3]. However, during the past decade only static properties of these systems have been considered. To our knowledge, the only experimental work on dynamic light scattering of FSSF [4] was carried out without systematic theoretical analysis. Hence a theoretical investigation on the dynamics of smectic-A liquid crystals in the presence of free surfaces can help us to gain deeper insight to the physics of FSSF and to provide a basis for understanding new experiments.

At free surfaces, smectic layers always orient parallel to the smectic/air interface [5]. When the system is driven out of equilibrium, surface and bulk elasticity and hydrodynamic effects give the film very complicated dynamical properties. In this paper we give the first theoretical calculation of the power spectrum of the surface fluctuations by studying the linearized hydrodynamic equations developed by Martin *et al.* [6]. We show that for thin films, the long wavelength surface fluctuations have two modes. The undulation mode is the dominant mode at low frequency and long wavelength. The peristaltic mode is expected to be very small. Only when the thickness of the film becomes very large does the peristaltic mode become comparable to the undulation mode. Permeation processes are important within the boundary layer [7,8] in order that the proper boundary conditions are satisfied. However, our calculation shows that the power spectrum of the surface fluctuations are independent of the permeation constant. We also show that the earlier experimental study of dynamic light scattering of FSSF [4] was performed in the limit of a very thin film such that the power spectrum has the same form as that of a soap film, *i.e.*, bulk elasticity makes no contribution to the power spectrum. The scaling relations suggested in Ref. [4] for the peak position are not valid in general, especially when the thickness of the film is increased, thus allowing the bulk elasticity of the smectic material to play a role in the dynamics. For a reasonably thick film, the power spectrum can have, in addition to a single undulation peak,

some additional structure which reveals the interaction between the two free surfaces and the contribution from bulk properties. We suggest that more light scattering experiments on a FSSF will be great help for an understanding of the interplay of the surface and bulk properties in this layered system.

In the ground state, an ideal smectic-A phase consists in a uniform piling of planar, parallel and equidistant layers of molecular thickness. We use a continuum description and take the average layer normals parallel to the z -axis. When small fluctuations are present, the bulk elastic free energy of smectic-A phase is given by [7]

$$F = \int d^3\mathbf{r} \frac{1}{2} \left\{ B \left(\frac{\partial u}{\partial z} \right)^2 + K_1 \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 \right\} \quad (1)$$

where $u(\mathbf{r}, t)$ is the layer displacement from the equilibrium position at position \mathbf{r} at time t , B and K_1 are, respectively, the the layer compression and undulation elastic moduli. The characteristic length $\lambda \equiv \sqrt{K_1/B}$ is typically of the order of the layer spacing ($\sim 10^{-7}$ cm) [7].

The equations for viscous flow in smectic A liquid crystals were first written down by Martin *et al* [6]. In the absence of topological defects, the system satisfies the equations of motion in bulk

$$\rho \frac{\partial v_i}{\partial t} = -\partial_i p + \partial_j \sigma'_{ij} + h \delta_{iz} \quad (2)$$

and

$$\frac{\partial u}{\partial t} = v_z + \zeta_p h \quad , \quad (3)$$

where σ' is the viscous stress tensor, ζ_p is the permeation constant and h is defined by

$$h \equiv \partial_i \left(\frac{\delta F}{\delta \partial_i u} \right). \quad (4)$$

In (2) we sum on repeated indices, and $\partial_j = \partial/\partial x_j$. An important length scale associated with permeation is the boundary layer δ . Within this distance to the boundary, permeation takes place to satisfy proper boundary conditions of the system under consideration [7–9].

We will show that the boundary layer is associated with the “permeation modes”. The boundary conditions for free surfaces are discussed below.

We consider a freely standing Smectic-A liquid crystal film with film normal in the z -direction. As noted, in equilibrium, the layers are parallel to the free surfaces. When the surfaces are perturbed by an external force, elastic forces and dissipative effects act to drive the system back to the equilibrium configuration. In this letter we study such a system by including the hydrodynamics in the film.

The geometry of the film is shown in Fig. 1; the film extends from $z = -d$ to $z = 0$ but is otherwise without boundaries in the x, y directions. We consider surface light scattering experiments with momentum transfer vector \mathbf{q} in the x -direction; we further assume translational invariance in the y -direction. The displacement of the upper and lower free surfaces from their equilibrium values are described by two functions $\zeta^+(x)$ and $\zeta^-(x)$.

We look for surface wave solutions with the form

$$v_z = \sum_k \left\{ A_k^+ e^{S_k q z} + A_k^- e^{-S_k q (z-d)} \right\} e^{i\omega t + i q x} \quad (5)$$

where $\text{Re}(S_k) \geq 0$. The $+$ ($-$) modes are the upper (lower) surface modes which have their maximum amplitudes at $z = 0$ ($z = -d$).

Two combinations of viscosities η' and η_3 [9] and a length scale $\kappa^{-1} \equiv \sqrt{\zeta_p \eta_3} \sim 10^{-7} \text{cm}$ [7–9] enter the analysis. A dimensionless frequency is conveniently defined as $\Omega = -\frac{i\omega\rho}{\eta_3 q^2}$. The characteristic frequency $K_1 q^2 / \eta_3$ for the decay rate of the bulk undulation mode, reduced by $\eta_3 q^2 / \rho$, yields a dimensionless frequency $\mu = \frac{K_1 \rho}{\eta_3^2}$. We assume incompressibility (the motion of the fluid is slow compared to the propagation of sound), long wavelength, *i.e.*, $(\kappa/q)^2 \gg 1$, $\lambda q \ll 1$. We consider low frequency satisfying conditions $\frac{\Omega}{\mu}(\lambda q)^2 \ll 1$, $\frac{\Omega^2}{\mu}(\lambda q)^2 \ll 1$. This means we consider a regime in which the velocity of the surface wave is slow compared to the typical velocity of “second sound”, $\sqrt{B/\rho}$ [7]. Furthermore, since then the frequency cannot be as large as $K_1 \lambda^{-2} / \eta_3$, permeation cannot have a significant contribution to the bulk undulation mode. [7] In this frequency and wavenumber domain we find three spatially decaying modes in the z -direction. One of them has long spatial relaxation length and

satisfies

$$S_3^2 = (\lambda q)^2 \left[\frac{\left(1 - \frac{\Omega}{\mu}(1 - \Omega)\right)}{1 + \frac{\Omega}{\mu} (\lambda q)^2 \left(\Omega - \frac{\eta'}{\eta_3} - 2\right)} \right] \quad (6)$$

$$\equiv (\lambda q)^2 [f(\Omega, q)]^2. \quad (7)$$

The other two modes (S_1 and S_2) are large compared to unity and satisfy

$$S^4 + \frac{\Omega}{\mu} (\kappa \lambda)^2 S^2 + \left(\frac{\kappa}{q}\right)^2 = 0. \quad (8)$$

In typical light scattering experiments $q \sim 10^2 - 10^4 \text{ cm}^{-1}$, $\omega \leq 10^8 \text{ rad/s}$. For typical materials $\eta_3 \sim 1 \text{ p}$ so that the long wavelength, low frequency conditions above are satisfied. Notice that when the denominator of the function $f(\Omega, q)$ defined above is significantly different from unity, we cannot separate the solutions for S_1 , S_2 , S_3 in the way mentioned above. The mode with relaxation S_3 is related to the dynamic generalization of the penetration length of layer distortion in the bulk due to surface undulation. [7,10] Following the terminology of Rapini, [10] from now on we refer to the S_3 -mode as the *elastic mode*. Since S_1 , and S_2 depend on the permeation constant, ζ_p , they are called *permeation modes*. For $e^{S_1 q d}$, $e^{S_2 q d} \gg 1$, i.e., $d \gg (S_1 q)^{-1}$, $(S_2 q)^{-1} \sim \delta$, the film thickness is large compared to the boundary layer δ (identified as the exponential decay length), and the permeation modes relax in the bulk.

The surface displacements ζ^+ , ζ^- satisfy the boundary condition for the normal component of the velocity in linear theory

$$\frac{\partial \zeta^{+(-)}}{\partial t} = v_z|_{z=0(-d)}. \quad (9)$$

The other boundary conditions can be understood from the covariant elasticity theory of smectic-A developed by Kléman and Perodi [11]. For free surfaces the normal components of the stress tensor as well as the normal component of the permeation force [12] should vanish. The condition that $\sigma_{xz} = 0$ on the free surfaces reveals $A_k^{+(-)} \ll A_3^{+(-)}$ for $k = 1, 2$, which indicates that the permeation modes have negligible contributions to the dynamics

of the system. The condition that $\sigma_{zz} = 0$ yields the following relation between the surface displacements and the external forces P_{ext}^+ , P_{ext}^- which are assumed to act on the free surfaces,

$$P_{ext}^{+(-)} = \left[p - \sigma'_{zz} + B \frac{\partial u}{\partial z} + \alpha \frac{\partial^2 \zeta^{+(-)}}{\partial x^2} \right]_{z=0(-d)}, \quad (10)$$

where α is the air-film surface tension. The normal component of the permeation force, in the system under consideration, is

$$B \frac{\partial u}{\partial z} = 0 \quad (11)$$

at $z = 0, -d$ for all x . The linear response function X connects the surface displacements with the external forces through

$$\zeta(q, w) = -\mathbf{X}(q, w) \mathbf{P}_{ext}(q, w) A, \quad (12)$$

where A is the surface area, ζ , \mathbf{P}_{ext} are vectors for surface displacement and external force respectively, e.g., $\zeta = (\zeta^+, \zeta^-)$; \mathbf{X} is a 2×2 matrix for the response function.

Putting Eqns. (11), (10), and (12) together our calculation leads to two surface dynamic modes; they are, respectively, the undulation mode with amplitude

$$\zeta^U = \frac{1}{2} (\zeta^+ + \zeta^-) \quad (13)$$

and the peristaltic mode with amplitude

$$\zeta^P = \frac{1}{2} (\zeta^+ - \zeta^-). \quad (14)$$

The response functions are in turn given by

$$X^U = \frac{1}{2\alpha q^2 A} \frac{1}{1 + g f(\Omega, q) \tanh\left(\frac{\lambda q^2 d}{2} f(\Omega, q)\right)}, \quad (15)$$

and

$$X^P = \frac{1}{2\alpha q^2 A} \frac{1}{1 + g f(\Omega, q) \coth\left(\frac{\lambda q^2 d}{2} f(\Omega, q)\right)}, \quad (16)$$

where $g \equiv \sqrt{BK_1}/\alpha$ measures the relative importance of bulk elasticity and surface tension. When the contribution from bulk elasticity and viscosity dominates, terms involving g are dominant. These equations are the central result of our calculation.

In the limit of infinite thickness, $d \rightarrow \infty$, the response functions of both modes become the same, indicating that the interactions between the two surfaces vanishes for large thickness. For low frequency ($\Omega \ll 100$) and infinite thickness, the result agrees with the earlier calculation by Rapini [10] for an infinitely thick smectic-A material with a free surface.

We now introduce a natural frequency of surface motion as $\omega_0^2 = \frac{2\alpha}{\rho d}q^2$, and dissipation coefficient $\gamma = \frac{\eta_3 q^2}{\rho}$. In the range of the only available experiment [4] (thin film, $d \sim 100$ nm, small wavenumber, $q \sim 10^4 \text{ cm}^{-1}$), $\lambda q^2 d f(\Omega, q)/2 \ll 1$. The response function is approximately

$$\begin{aligned} X^U &\sim \frac{1}{1 + \frac{1}{2}g [f(\Omega, q)]^2 \lambda q^2 d} \\ &\sim \frac{1}{(\omega_0^2 - \omega^2) + i\gamma\omega}, \end{aligned} \quad (17)$$

which is the same as the response function of a damped driven simple harmonic oscillator. The peak position in the range of weak damping ($\frac{\eta_3 q^2}{\rho}\omega \ll \sqrt{\frac{2\alpha}{\rho d}}q$) is

$$\omega = q \sqrt{\frac{2\alpha}{\rho d}} \quad (18)$$

This is the same as for a soap film and gives the scaling relation which the experimental data satisfy. In general we may not have a system with weak damping, and the peak position should be slightly modified. On the other hand, the width of the undulation mode peak ($\eta_3 q^2/\rho$) does provide information about the viscosity η_3 .

The peristaltic mode changes the layer spacing much more significantly than the undulation mode; hence we expect that the peak in the peristaltic power spectrum occurs when the term proportional to g in Eq. (16) dominates. Also in the range that we are interested in, the relation $\Omega/\mu \gg 1$ is valid. A straightforward calculation leads to an estimate of the peak position of the peristaltic mode :

$$\lambda q^2 d f_I(\Omega, q) \approx \pi \quad (19)$$

where $f_I(\Omega, q)$ is the imaginary part of the function f we have defined via Eq. (7). In this approximation the surface tension plays no role in peristaltic mode, the peak position is essentially independent of g and has the form

$$\Omega \approx -i \frac{2\mu\pi^2}{\lambda q^2 d \sqrt{\lambda^2 q^4 d^2 + 4\mu\pi^2}}. \quad (20)$$

For typical material parameters the above approximation yields the peristaltic peak within 5%. From this relation we can estimate the bulk elastic coefficients K_1 and B by fitting the value μ and λ from the peristaltic peak.

One may ask whether it is possible to observe the peristaltic mode and the special features of a smectic-A liquid crystal in a free-standing film experiment. Figure 2 shows the power spectrum of one free surface, *i.e.*, $\zeta^U + \zeta^P$, for a typical choice of parameters with increasing film thickness. As the film gets thicker we observe that a peak develops in the higher frequency range. This peak is due to the peristaltic mode. When $L = qd \geq 12$, i $\Omega \geq 3$ there is some extra structure arising from sources other than the peristaltic mode. Figure 3 shows the power spectrum for the same choice of parameters with $qd = 15$. The contribution from both undulation and peristaltic modes are plotted in long and short dashed lines, respectively. We find that the power spectrum of the peristaltic mode is about one order of magnitude smaller than the contribution of the undulation mode. Notice that there is a second peak of the undulation mode in the high frequency region. It comes from the oscillating behavior of the hyperbolic tangent function when the argument $(\lambda q^2 d f(\Omega, q)/2)$ is complex. This extra structure in the power spectrum at high Ω is a result of the interplay of bulk elasticity and the existence of the two free surfaces; it is a special feature of a structured fluid. Hence we conclude that for reasonable choices of material parameters and for an experiment with typical dynamic range, it should be possible to observe the peristaltic mode. Combinations of material parameters can be extrapolated from the shape of the undulation peak and the peristaltic peak. However, the detailed shape of the power spectrum is sensitive to the specific material parameters used in a laboratory experiment.

In conclusion, we have derived the power spectrum of a freely standing smectic-A film

within linear hydrodynamics and assuming the absence of topological defects. The dynamics of this system are dominated by the elastic mode and the permeation constant does not show up in the power spectrum of the surfaces. The permeation process is important near the surfaces and helps the system to satisfy proper boundary conditions. When the thickness of the film is small enough, bulk elasticity does not contribute to the undulation mode, and the peristaltic mode is not observable. However, for a reasonably thick film the power spectrum does show the interplay of surface tension and bulk elasticity. The extra structure in the power spectrum is a special feature due to the existence of two free surfaces and the contribution from the bulk elasticity. We suggest that further experimental work on FSSF over a wider range of film thickness and wavenumber can observe these interesting features.

We thank Prof. X-l. Wu and D. Dash for very helpful discussions, and Prof. Takao Ohta for his interest and assistance. H.Y.C. acknowledges financial support from University of Pittsburgh as an Andrew Mellon Predoctoral Fellow. D.J. is grateful for the support of the NSF under DMR9297135.

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Figure Caption

Figure 1. Schematic of a freely standing smectic-A film of thickness d .

Figure 2. The power spectrum (natural logarithm) for a typical choice of parameters with increasing thickness of the film: $\lambda q = 10^{-3}$, $\mu = 10^{-4}$, $g = 0.1$, $\eta' = \eta_3$. $L = qd$ is dimensionless. As the thickness increases, we can easily see the peristaltic mode and extra structure of the undulation mode provide additional contribution to the power spectrum.

Figure 3. The power spectrum (natural logarithm) for a typical choice of parameters: $\lambda q = 10^{-3}$, $qd = 15.0$, $\mu = 10^{-4}$, $g = 0.1$, $\eta' = \eta_3$. The long dashed line is the undulation mode, short dashed line is the peristaltic mode, solid line is the total power spectrum. Notice that there is a small peak in the undulation mode at $i \Omega \sim 4$.

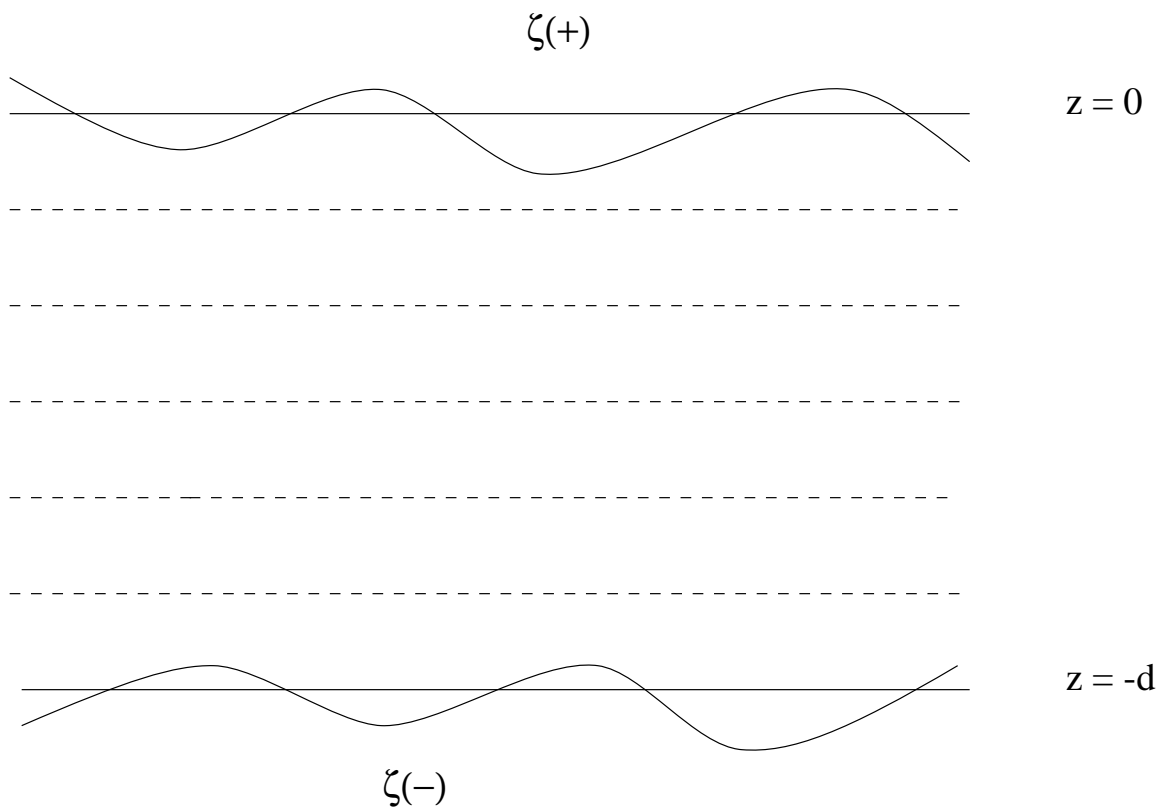


Figure 1

Figure 2

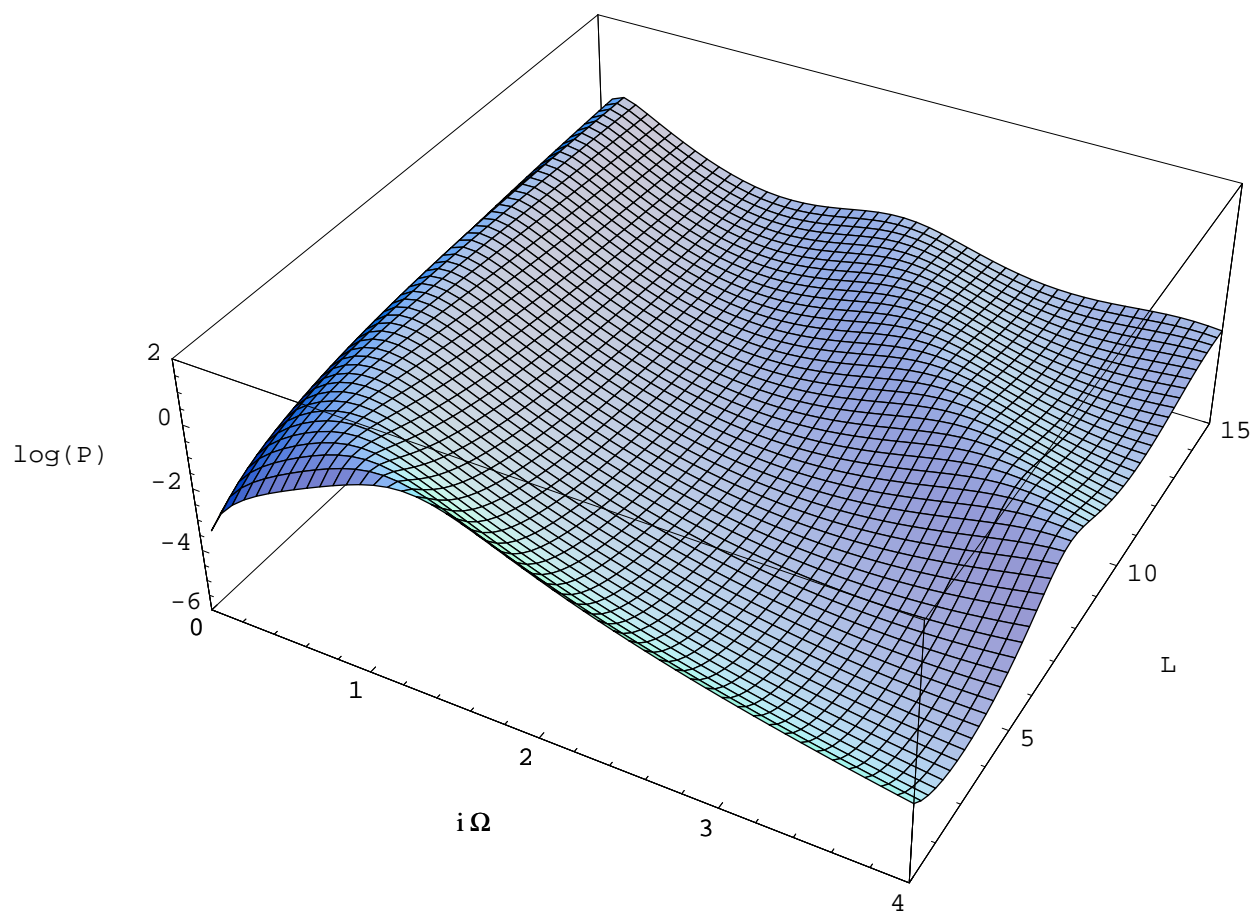


Figure 3

